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**EUROPEAN PATENT APPLICATION**

21 Application number: 88306510.4

51 Int. Cl. **C 22 B 34/12**  
**C 22 B 5/04**

22 Date of filing: 15.07.88

30 Priority: 17.07.87 JP 177014/87  
31.07.87 JP 190186/87

43 Date of publication of application:  
18.01.89 Bulletin 89/03

64 Designated Contracting States: DE FR GB IT SE

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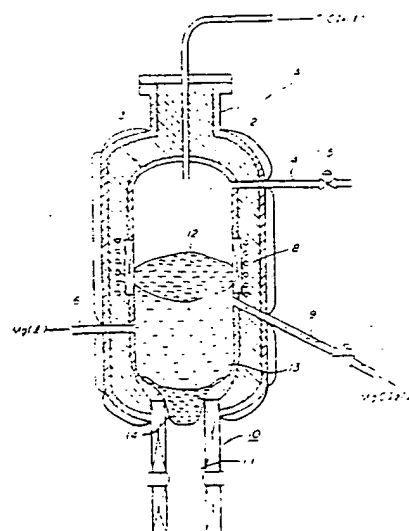
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54 Method for producing metallic titanium and apparatus therefor.

57 A method for producing metallic titanium (34) by the reduction of titanium tetrachloride with a reducing metal agent, capable of continuously producing metallic titanium on an industrial scale. The temperature and pressure of the reaction zone (12) are kept above the melting point of metallic titanium and at least above the vapour pressure of the reducing metal agent, respectively, so that the reducing metal agent and its chloride (13) may be kept in a molten state but without boiling.

FIG. 1



## Description

## METHOD FOR PRODUCING METALLIC TITANIUM AND APPARATUS THEREFOR

This invention relates to a method for producing metallic titanium and an apparatus therefor, and more particularly to a method and apparatus for producing metallic titanium from titanium tetrachloride at a reaction temperature above the melting point of titanium.

In the known "Kroll" method, metallic titanium is produced by the reduction of titanium tetrachloride by metallic magnesium.

In the Kroll method, the reduction reaction is generally carried out at a temperature below the melting point of metallic titanium while keeping the reduction vessel at normal or reduced pressure to produce spongy metallic titanium. The spongy metallic titanium product is subjected to vacuum separation or leaching to remove any excess metallic magnesium and magnesium chloride (by-product) remaining in the fine internal voids of the metallic titanium product and is thus purified. The purified metallic titanium is then crushed and formed into a shape suitable for melting. After melting, an ingot of titanium is formed.

As can be seen, the Kroll method is a batch type process. Accordingly, producing the metallic titanium ingot according to the Kroll method requires at least four discontinuous or independent steps comprising a reduction reaction step, a vacuum separation step, a crushing step and a melting step.

The Kroll method also has the following disadvantages.

The spongy metallic titanium which is the reaction product is firmly adhered to a reduction reaction vessel, so that much labour and time are required for peeling the adhered reaction product from the vessel.

Another disadvantage is that it is very difficult to remove the heat of reaction from the reaction system during the reduction step sufficiently rapidly.

A further disadvantage is that the titanium is produced at a sufficiently elevated temperature to increase its activity. Accordingly, it is readily polluted with the material of the reaction vessel wall.

Still another disadvantage is that the separation step for purification of the titanium requires much attention in order to prevent contamination of the titanium with moisture, air and the like. Accordingly, removal of the unreacted material and the by-product must be carried out in a vacuum or argon atmosphere.

For the purpose of reducing metal halide with a reducing metal agent without using the Kroll method other methods are proposed in each of which the reduction reaction is carried out at a reaction temperature above the melting point of the metal to be produced and the product is continuously removed from the reaction vessel. The metal product is then obtained in a molten state or in the form of an ingot by cooling the molten metal product for solidification.

As an example, Japanese Patent Application Laying-Open Publication No.35733/1981 discloses a method for producing metallic titanium which comprises the steps of introducing titanium chloride and a reducing metal agent both in the vapour state into a reaction vessel to react both under conditions so that a liquid metallic titanium product is obtained together with the chloride of the reducing metal agent in the form of a vapour. The chloride by-product of the reducing metal agent is separated from the titanium product for recovery and the metallic titanium product is solidified in a mould kept at a temperature below the melting point of the metallic titanium product to obtain an ingot which is removed from the reaction vessel.

Japanese Patent Publication No.19761/1971 discloses a method for producing metal comprising the steps of introducing titanium tetrachloride vapour and a liquid reducing metal agent into liquid metal in a reaction vessel, heating a reaction zone to a temperature above the melting point of titanium to obtain a metallic titanium product and a chloride by-product of the reducing metal agent in a molten state under a vapour pressure of the reducing metal agent at the relevant temperature, separating the product and by-product from each other using the difference in their gravities, and separately removing them from the reaction vessel.

Various similar methods have attempted to solve the problems of the Kroll method by reducing the metal halide with the reducing metal agent while keeping the reaction temperature above the melting point of the metal product to obtain the molten metallic titanium product. However, while these methods are disclosed in the patent literatures, they have not been commercialised on an industrial scale. The reason is believed to be that it is very difficult to select a material for the reaction vessel which withstands a sufficiently high temperature to produce active metal of a high melting point such as titanium, zirconium or the like in the reaction vessel and to keep it in a molten state.

More particularly, for example, the method taught in Japanese Patent Publication No.19761/1971 is to reduce titanium tetrachloride with magnesium to produce metallic titanium while keeping the temperature in the reaction zone at about 1730°C and the pressure in the reaction vessel at about 5 atms corresponding to a partial pressure of the magnesium chloride by-product at that temperature to produce the metallic titanium product and the magnesium chloride by-product in a molten state. Thus, in the method the reaction zone temperature is about 1720°C and its pressure is about 5 atms which is substantially equal to the vapour pressure of the magnesium chloride, produced in liquid form. This results in the magnesium boiling which leads to a failure to maintain the magnesium in an amount sufficient to reduce titanium tetrachloride in the reaction zone fully. This causes the reaction to take place in the presence of insufficient magnesium which often produces lower chlorides of titanium such as titanium trichloride, titanium dichloride and the like.

Also, in this method, the reactants (titanium tetrachloride in the form of a gas and magnesium in the form of a liquid) are supplied through graphite pipes to a molten layer of the reaction product the bottom of the

reaction vessel to carry out the reaction in the molten layer. This causes the open end of the graphite pipes to be corroded by the active molten titanium product. Also, the molten titanium product contacts each of the reactants at a relatively low temperature at the open end of the pipes, solidifying the reactants and so clogging the pipes. Furthermore, since the reaction is a reduction reaction taking place in the molten layer of titanium, the titanium product is contaminated with unreacted reactants, the by-product and the like. Moreover, the lack of magnesium in the reaction zone leads to a decrease in reaction efficiency per a reaction sectional area.

It is an object of the present invention to provide a method and apparatus for producing metallic titanium by the reduction of titanium tetrachloride by a reducing metal agent which are capable of continuously producing metallic titanium at a lower energy cost and on an industrial scale.

According to one aspect of the invention, there is provided a method for producing a metal (e.g. titanium) by the reduction of the product metal (e.g. titanium) tetrachloride with a reducing metal agent characterised by the steps of: maintaining the temperature and pressure in a reaction zone in a reaction vessel above the melting point of the product metal (e.g. metallic titanium) to be produced and above the vapour pressure of the reducing metal agent at that temperature; supplying the product metal (e.g. titanium) tetrachloride and the reducing metal agent to the reaction vessel to react to produce the product metal (e.g. a metallic titanium) and a chloride by-product of the reducing metal agent while maintaining the product and the by-product in a molten state; separating the product metal (e.g. metallic titanium) and the chloride by-product of the reducing metal agent from each by making use of the differences in their densities; collecting the product metal (e.g. metallic titanium) at the bottom of the reaction vessel; and continuously drawing out the product metal (e.g. metallic titanium) from the bottom of the reaction vessel.

Preferably, the titanium product is solidified by cooling as it is withdrawn.

Preferably, a molten bath of chloride of the reducing metal agent and optionally also of the reducing metal agent itself is previously formed in the reaction vessel so that the surface of the molten bath constitutes the reaction zone and titanium tetrachloride and the reducing metal agent are supplied to the reaction zone. Preferably the titanium tetrachloride is supplied in liquid form from the top of the reaction vessel and the reducing metal agent is supplied either in the same way or is injected into the bath.

Preferably, the chloride by-product of the reducing metal agent is discharged from the reaction vessel at a rate arranged to maintain the position of the reaction zone substantially constant. The method may also include the steps of inserting a titanium ingot into the bottom of the reaction vessel resulting in the coalescence of the separated metallic titanium metal product with the titanium ingot and drawing the metallic titanium product out continuously together with the titanium ingot at a rate corresponding to the amount of the metallic titanium product being coalesced with the titanium ingot.

According to another aspect of the invention, there is provided an apparatus for producing metallic titanium by the reduction of titanium tetrachloride with a reducing metal agent characterised by: a reaction vessel having a reaction zone in which a temperature above the melting point of the titanium product is defined and which is kept at a pressure sufficient to prevent boiling of the reducing metal agent and its chloride at that temperature; a reducing metal agent feed pipe for supplying the reducing metal agent in the form of a liquid from the side or the top of the reaction vessel to the reaction zone; a titanium tetrachloride feed pipe for supplying titanium tetrachloride from the top of the reaction vessel to the reaction zone; a discharge pipe for discharging the chloride by-product of the reducing metal agent from the side of the reaction vessel; heating means arranged outside the reaction vessel at a position corresponding to the reaction zone and a withdrawing section at the bottom of the reaction vessel for continuously drawing out the metallic titanium product.

One preferred embodiment of the invention includes a reaction vessel made of thick titanium plate in which a reaction zone is defined and which is kept at a pressure sufficient to prevent boiling of the reducing metal agent and its chloride. A reducing metal agent feed pipe supplies the reducing metal agent in the form of a liquid from the side or top of the reaction vessel to the reaction zone, and a titanium tetrachloride feed pipe supplies titanium tetrachloride from the top of the reaction vessel to the reaction zone. A discharge pipe for discharging a chloride by-product of the reducing metal agent extends from the side of the reaction vessel. Heating means are arranged outside the reaction vessel at a position corresponding to the reaction zone for carrying out electromagnetic induction heating, resistance heating or the like, and a mould section is arranged at the bottom of the reaction vessel for solidifying the molten metallic titanium product by cooling and continuously drawing out it from the reaction vessel.

An alternative reaction vessel structure includes a reaction vessel made of metal such as copper or a ceramic material such as alumina, zirconia or the like in which a reaction zone is defined and which is kept at a pressure sufficient to prevent boiling of the reducing metal agent material and its chloride. The reaction vessel has a vertically extending hollow shape and is open at the top and bottom. The reaction vessel includes a cooling agent circulating path for cooling the inner surface of the reaction vessel and portions of its outer periphery at a position corresponding to the reaction zone. The vessel also includes a removal section with heating means for heating a molten material which carries out electromagnetic induction heating, resistance heating or the like.

In the present invention, a suitable reaction vessel provided with the heating means may comprise a crucible, as disclosed in U.S. Patent No. 3,755,091 which is adapted to melt titanium chips, titanium sponge or the like for preparing a titanium ingot and is used in an evacuated inert atmosphere. Such a crucible may be incorporated in a pressure vessel for use as the reaction vessel in the present invention which includes the

reaction zone for reducing titanium tetrachloride and the mould section for solidifying the metallic titanium product by cooling and continuously removing it therefrom.

The present inventors have conducted the following reaction test in order to evaluate the reaction efficiency for reducing titanium tetrachloride with metallic magnesium according to the present invention.

## REACTION TEST

A pressure in the reaction vessel was kept at 50 atms. The reaction vessel was charged with 845g metallic magnesium, which was heated to 1350°C by electromagnetic induction heating or resistance heating to form a molten magnesium bath in the reaction vessel. Immediately after the heating, 1340g liquid titanium tetrachloride was fed to the molten magnesium for 50 seconds at a feed rate of 1608g/min.

The temperature of the bath reached the melting point of titanium in 15 seconds after the beginning of the addition of titanium tetrachloride, thereby producing liquid titanium. The yield of titanium was 99% and the reaction efficiency per unit sectional area of the reaction vessel was 62.7 kmol/hr m<sup>2</sup>. For comparison, the Kroll method was carried out and was found to give a reaction efficiency per unit sectional area of a reaction vessel of 1.3 kmol/hr m<sup>2</sup>.

The efficiency of reaction between titanium tetrachloride and metallic magnesium in the gas phase is calculated in an article entitled "Gas Phase Reaction Test Report" by Professor Takeuchi of Tohoku University, Journal of Japan Institute of Metals, 23, pp625-637 (1965), as follows:

In the reaction test, the volume of a titanium ribbon for growing titanium on was 0.057m<sup>3</sup> and the deposition rate of titanium on to the titanium ribbon was 3.45kg/hr (72mol/hr). Accordingly, its volume efficiency is  $72/0.057 = 1263\text{mol/hr m}^3$  and its reaction efficiency per area is 1.263kmol/hr m<sup>2</sup>.

It may not be strictly fair simply to compare the reaction efficiency of the present invention to the reaction efficiency calculated in this way because reaction conditions such as temperature, a feed rate of feedstocks and the like were set differently. However, it will be noted that the reaction between the titanium tetrachloride and metallic magnesium in the present invention exhibits a reaction efficiency at least 49.6 (62.7/1.263) times that of the above described gas phase reaction and 48.2 (62.7/1.3) times as much as that of the Kroll process. The fact that the present invention exhibits such a higher reaction efficiency is believed to be due to the liquid metallic magnesium and liquid titanium tetrachloride being supplied to the reaction zone kept there at a high temperature and a high pressure.

The temperature of the reaction zone is set above the melting point of titanium. In order to precipitate stably the metallic titanium product onto the bottom of the reaction vessel while keeping it in a molten state, it is desirable to keep the reaction vessel at a temperature which is about 100-200°C higher than the melting point of titanium and to keep the pressure of the reaction zone at least above the vapour pressure of the reducing metal agent at the reaction temperature and preferably above the sum of the vapour pressures of the reducing metal agent and its chloride.

More preferably, when titanium (melting point of 1670°C) is to be produced using titanium tetrachloride as the feedstock and magnesium as the reducing metal agent, the bath in the reaction vessel is kept at a temperature of at least 1670°C and more preferably 1827°C, and at a pressure above 42.6 atms, corresponding to the partial pressure of magnesium and more preferably above 48.6 atms corresponding to the total sum of the partial pressure of magnesium (42.6

For reduction of titanium tetrachloride, the reducing metal agent may be used in a stoichiometric amount. However, in order to carry out the reduction fully, it is desirable to use a predetermined excess of the reducing metal agent in the reaction zone to inhibit the production of lower titanium chlorides.

The invention may be carried into practice in various ways and some embodiments will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a vertical section through a first embodiment according to the present invention;

Figure 2 is a view similar to Figure 1 showing a second embodiment; and

Figure 3 is a partially cutaway perspective view generally showing an example of a reaction vessel incorporated in the apparatus shown in Figure 2.

In the present invention, titanium tetrachloride and a reducing metal agent are supplied in liquid form to a reaction zone for reaction. Magnesium or sodium may be used as the reducing metal agent.

The apparatus shown in Figure 1 includes a reaction vessel structure A which also serves as a pressure vessel. The reaction vessel structure A includes an outer shell or outer wall 1 made of a steel plate, an inner wall made of titanium serving as a reaction vessel 3 and a heat insulating material 2 between the outer shell 1 and the reaction vessel 3.

An inert gas (e.g. argon) is introduced to the reaction vessel 3 from a pressure adjusting pipe 4 through a valve 5, so that the interior of the reaction vessel 3 is set and kept at a pressure sufficient to prevent substantially any boiling of the magnesium and vessel 3 is set and kept at a pressure sufficient to prevent substantially any boiling of the magnesium and magnesium chloride, even when the temperature in a reaction zone defined in the reaction vessel 3 rises above the melting point of titanium. For example, the reaction vessel 3 is kept at a pressure of about 50 atms when the temperature of the bath in the reaction vessel 3 is 1827°C. When the pressure in the reaction vessel 3 is above or below the set value, an automatic pressure adjusting valve (not shown) is operated to keep the pressure at the set value automatically.

Liquid magnesium for use as the reducing metal agent is supplied to the reaction zone through a reducing

metal agent feed pipe 6 extending through the side wall of the reaction vessel structure A and into the reaction vessel 3. Similarly, liquid titanium tetrachloride is supplied to the reaction zone through a titanium tetrachloride feed pipe 7 extending through the top of the reaction vessel structure A and into the vessel 3.

The reaction vessel 3 is provided at an intermediate part of its outer periphery (in a vertical direction) surrounding the reaction zone with a heater or heating means 8 adapted to carry out electromagnetic induction heating, resistance heating or the like to adjust the temperature of the reaction zone in the reaction vessel 3 to a level above  $1670^{\circ}\text{C}$ , corresponding to the melting point of titanium. A discharge tube 9 is connected to the reaction vessel 3 adjacent to the heating means 8 for discharging magnesium chloride by-product formed by the reduction reaction.

A mould section 10 for solidifying the molten metallic titanium product is connected at the bottom of the reaction vessel, for cooling and drawing out the titanium product.

The production of metallic titanium using the apparatus shown in Figure 1 will now be described.

Firstly, a titanium ingot 11 is inserted in the mould section 10 to close the bottom of the reaction vessel 3 and then magnesium and magnesium chloride are charged in small amounts into the reaction vessel 3. The atmosphere in the reaction vessel 3 is replaced with argon gas and then the heater 8 is operated to melt the magnesium and magnesium chloride, resulting in a molten bath of magnesium and magnesium chloride being formed in the reaction vessel 3. The molten magnesium 12 floats above the magnesium chloride due to the difference in their densities, so that it may remain separate from the magnesium chloride.

Subsequently, more argon gas is introduced into the reaction vessel 3 to increase the pressure. Then, liquid titanium tetrachloride is fed to the surface of the molten magnesium 12 through the titanium tetrachloride feed pipe 7 connected to the top of the reaction vessel 3. Liquid magnesium is supplied to the molten magnesium chloride through the magnesium feed pipe 6 connected to the side of the reaction vessel 3. Alternatively, the magnesium feed pipe 6 may be connected to the top of the reaction vessel 3 so that both the titanium tetrachloride and the magnesium may be supplied in liquid form from the top of the reaction vessel 3 to the reaction zone (as in the apparatus of Figure 2 described hereinafter).

Titanium tetrachloride supplied to the surface of the molten magnesium layer of the bath reacts as a liquid with the liquid magnesium to produce titanium 14 and magnesium chloride 13. Alternatively, it may react as a vapour with magnesium vapour vapourised from the molten magnesium phase of the bath or indeed with liquid magnesium.

The heat of reaction and the effect of the heater 8 cause the temperature of the molten bath in the reaction vessel 3 to rise above the melting point of titanium. However, the reaction vessel 3 is kept at a pressure above the vapour pressure of magnesium at that temperature, so the titanium product 14, the magnesium chloride by-product 13 and the magnesium 12 are all kept in a liquid state. Also, the molten bath is vertically separated into three layers, namely magnesium 12, magnesium chloride 13 and titanium 14, in that order, due to the differences in their densities.

The molten metallic titanium product 14 precipitates and sinks through the molten magnesium layer and the molten magnesium chloride layer to the bottom of the reaction vessel 3 and reaches the top of the titanium ingot 11 to coalesce with it as it is produced. Correspondingly, the titanium ingot 11 is continuously drawn out at a suitable rate, during which the titanium is solidified by cooling.

The magnesium chloride by-product 13 is discharged through the discharge pipe 9 connected to the side of the reaction vessel 3 at a discharge rate which is adjusted so that the molten bath in the reaction zone is kept constant in depth. The titanium ingot 11 is drawn out at a rate corresponding to the amount of titanium precipitated on the titanium ingot (or the precipitation rate of the titanium) by means of rollers (not shown). Accordingly, the position of the molten titanium product above the titanium ingot 11 is kept substantially constant.

The apparatus shown in Figures 2 and 3 is constructed in substantially the same manner as that of Figure 1 except for the construction of the reaction vessel 3, the arrangement of the reducing material feed pipe 6 and the construction of the heater or heating means 8.

More particularly, the reaction vessel 3 is formed as a vertically extending cylindrical shape, the top and bottom of which are open and is divided into two or more segments 32 by means of vertical slits 31 in the wall of the reaction vessel 3. In the illustrated embodiment, it is divided into twelve segments 32. Each of the segments 32 is formed of a material of good thermal conductivity for example, a metal such as copper or the like. The slits 31 are filled with an electrically insulating and heat resistant material to insulate the segments 32 from one another electrically. The segments 32 are each provided with an internal cooling pipe 33 for supplying a cooling agent through them to cool the wall of the reaction vessel 3 defining the reaction zone therein. The cooling pipes 33 are connected to one another and between a cooling agent inlet 34 and a cooling agent outlet 35 to form a path for circulating a cooling agent.

An upwardly extending duct 15 is connected to the open top end of the reaction vessel, the upper end of which is connected to the exterior through a cylinder section 16 and in which the reducing agent feed pipe 6 is located. The titanium tetrachloride feed pipe 7 is positioned within the upper portion of the reaction duct 15. Thus, liquid magnesium and liquid titanium tetrachloride are supplied through the feed pipes 6 and 7 to the reaction zone. The reaction vessel 3 is provided at a bottom thereof with a mould section 19, through which a titanium ingot 11 is inserted into the reaction vessel 3.

The reaction vessel 3 constituted by the segments 32 has at its upper part on the outer periphery at a position corresponding to the reaction zone in the reaction vessel 3, an upper electromagnetic induction

heating coil 8a for raising a temperature of the reaction zone above the melting point of titanium (or 1670°C). On its lower part, the vessel 3 has a lower electromagnetic induction heating coil 8b for melting the top of the titanium ingot 11 and the magnesium chloride adjacent the top to keep the top of the ingot constantly in a molten state during the reaction. Thus, in the illustrated embodiment, the heating means 8 comprises the upper and lower electromagnetic induction heating coils 8a and 8b.

As described above, the embodiment of Figures 2 and 3 is so constructed that the reaction vessel 3 is divided into a plurality of the cooled segments 32 and the segments 32 are electrically insulated from one another by the slits 31. Such a construction substantially prevents the generation of eddy currents in each segment 32 due to electromagnetic induction heating thereby permitting the molten materials in the reaction zone of the reaction vessel 3 and the top of the titanium ingot to be subjected to induction heating without heating the segments 32. The apparatus includes a discharge pipe 9 for discharging the magnesium chloride by-product which is connected to a substantially central portion of a side of the reaction vessel, in this case between the upper and lower heating coils 8a and 8b.

In the illustrated embodiment, the reaction vessel 3 is made of a metal agent in view of economic efficiency and maintenance. However, it may be formed of a ceramic material such as alumina, zirconia or the like. In such a case, it would not be necessary to divide the reaction vessel 3 into segments.

The operation of the apparatus shown in Figures 2 and 3 will now be described. Basically, operation of the apparatus of Figures 2 and 3 is similar to that of Figure 1.

First, a titanium ingot 11 is inserted into the mould section 10 to close the bottom of the reaction vessel 3 and then magnesium and magnesium chloride are charged in small amounts into the reaction vessel 3. Then, the atmosphere in the reaction vessel 3 is replaced with argon gas and the lower magnetic induction heating coil 8b is operated to melt the top of the titanium ingot 11 while the upper magnetic induction heating coil 8a is operated to melt the magnesium and magnesium chloride charged into the reaction zone, resulting in a molten bath of magnesium and magnesium chloride being formed in the reaction vessel 3. Molten magnesium 12 collects and floats above the magnesium chloride due to the difference in their densities and the magnetic field by electromagnetic induction, so that it remains separate from the magnesium chloride. Part of the molten magnesium chloride flows into the gap between the titanium ingot 11 and the inner surface of the reaction vessel 3 where it solidifies by cooling, to give pressure sealing and electrical insulation actions.

Subsequently, more argon gas is introduced into the reaction vessel 3 to increase the pressure, and liquid magnesium and titanium tetrachloride are fed through the magnesium feed pipe 6 and the titanium tetrachloride feed pipe 7 connected to the top of the reaction vessel 3 to the surface of the molten magnesium 12, forming an upper layer of the molten bath or the reaction zone. Alternatively, the magnesium feed pipe 6 may be connected to the side of the reaction vessel 3 as in the apparatus of Figure 1.

Titanium tetrachloride in the reaction zone or at the surface of the molten magnesium layer of the molten bath reacts in liquid form with the liquid magnesium to produce titanium 14 and magnesium chloride 13. Alternatively, it may react as vapour with magnesium vapour vapourised from the molten magnesium layer or with liquid magnesium.

The heat of reaction and the effect of the heater 8 cause the temperature of the molten bath in the reaction vessel 3 to rise above the melting point of titanium. However, the reaction vessel 3 is kept at a pressure above a vapour pressure of magnesium at that temperature, so that the titanium product 14, the magnesium chloride by-product 13 and the magnesium 12 are all kept in a liquid state. Also, the molten bath is vertically separated into three layers, namely, magnesium 12, magnesium chloride 13 and titanium 14, in that order, due to the differences in their densities.

The molten metallic titanium product 14 precipitates and sinks through the molten magnesium layer and the molten magnesium chloride layer to the bottom of the reaction vessel 3 and reaches the top of the titanium ingot 11, where it remains in the molten state and is subjected to stirring and mixing by the lower electromagnetic induction heating coil 8b. This results in the molten titanium product 14 being homogeneous.

The titanium product 14 coalesces with the top of the titanium ingot 11 and the titanium ingot 11 is continuously drawn out at a suitable rate, during which the product is cooled and solidified by the cooling agent circulated in the cooling pipes 33 of the segments 32.

The magnesium chloride by-product 13 is discharged through the discharge pipe 9 connected to the side of the reaction vessel 3 at a discharge rate which is adjusted so that the molten bath at the reaction zone is kept at a constant level. At this time, a part of the magnesium chloride flows into the gap between the titanium ingot 11 and the wall of the reaction vessel and solidifies there to form an insulating layer which serves to prevent contact between the ingot 11 and the reaction vessel. The insulating layer exhibits heat insulating and pressure sealing actions. The insulating layer may be partially broken by mechanical friction when the titanium ingot 11 is downwardly drawn out, however, when this happens, the magnesium chloride rapidly flows from the molten magnesium chloride phase into the broken portion of the insulating layer and solidifies to re-form an insulating layer. Also, the molten titanium is heated by the lower electromagnetic induction heating coil 8b and tends to levitate at its central portion. Accordingly, magnesium chloride readily flows into the gap between the wall of the reaction vessel and the titanium ingot 11 to facilitate formation of the additional insulating layer.

The titanium ingot 11 is drawn out at a rate corresponding to the amount of titanium precipitated on the titanium ingot by precipitation by means of rollers (not shown). Accordingly, the position of the molten titanium product above the titanium ingot 11 is kept substantially constant. A part of heat of reaction in the reaction vessel is removed upwards from the reaction vessel 3 by radiation and convection, however, a large part of the

heat is removed outwardly by the cooling agent circulated in the circulation pipes 33 at the segments 32 constituting the reaction vessel 3.

Accordingly, the present invention is carried out under conditions where the temperature of the reaction zone is kept above the melting point of the metallic titanium product and its pressure is kept at least at the vapour pressure of the reducing metal agent at that temperature, so that boiling of the reducing metal agent and its chloride may be substantially prevented to keep them in a liquid state in the reaction vessel, resulting in the reduction being carried out efficiently.

The present invention also allows the metallic titanium to be produced in the form of a liquid if preferred. The separation of the metallic titanium product and the chloride by-product of the reducing metal agent is simple, as is the recovery of the by-product, and the titanium ingot may be directly removed, enabling the whole production apparatus to be small-sized.

Furthermore, the present invention permits production of metallic titanium to be continuously carried out, so that the separating, crushing and melting steps required in the conventional Kroll process may be eliminated, leading to a significant decrease in producing costs while providing titanium of the highest quality.

The above description has been made in connection with manufacturing titanium. However, the present invention can also be applied to production of metals such as zirconium, hafnium, niobium and their alloys, silicon, and the like.

The present invention will now be illustrated with reference to the following non-limiting Examples.

#### EXAMPLE 1

The example was carried out using an apparatus constructed in accordance with Figure 1.

A reaction vessel having an inner diameter of 20cm was used and a titanium ingot having an inner diameter of 10cm was inserted into the mould section of the reaction vessel to close the bottom. 20kg magnesium chloride and 4.6kg magnesium were charged into the reaction vessel, which was then fully closed.

The atmosphere in the reaction vessel was replaced with argon, the magnesium chloride and magnesium were heated to 1000°C by electromagnetic induction heating and the reaction vessel was pressurised to about 50atms.

Immediately after such conditions were established, titanium tetrachloride and liquid magnesium kept at 800°C were supplied to the reaction vessel at feed rates of 4.0ℓ/min (7.0kg/min) and 1.2ℓ/min (1.8kg/min), respectively. This caused a temperature of the bath to rise rapidly to 1827°C, and so the power for the electromagnetic induction heating was decreased to keep the temperature at 1827°C ± 50°C.

Subsequently, the ingot was drawn out downwardly at an average velocity of 4.9cm/min. The operation was continued for 3 hours, resulting in a titanium ingot being manufactured in an amount of 0.3 tonne.

The magnesium chloride by-product produced during the operation was continuously discharged from the reaction vessel at the appropriate rate to keep the depth of the bath in the reaction vessel constant.

The titanium ingot so produced was compared to sponge titanium produced by the Kroll process. It was found that the titanium ingot had a high purity and quality as indicated in Table 1, in which the figures are in wt% and the balance is titanium in each case.

Table 1

Type	Chemical Composition										
	O	C	H	N	Si	Fe	Al	Cr	Ni	Cu	Sn
Present Invention	0.010	0.005	≥0.001	0.001	0.007	≥0.010	0.006	≥0.001	≥0.005	0.005	0.01
Sponge Ti by Kroll Method	≥0.06	≥0.01	≥0.003	≥0.01	≥0.02	≥0.05	≥0.03	≥0.01	≥0.02	≥0.005	≥0.02

The Symbol  $\geq$  is used to mean "up to and including", so that the following figure is a maximum value



**EXAMPLE 2**

This example was carried out using an apparatus constructed in accordance with Figures 2 and 3.

A reaction vessel having an inner diameter of 20cm was used and a titanium ingot having an inner diameter of 19.5cm was inserted into the mouth section of the reaction vessel to close the bottom. Then, 20kg magnesium chloride and 4.6 kg magnesium were charged into the reaction vessel, which was then fully closed.

The atmosphere in the reaction vessel was replaced with argon and the top of the titanium ingot and the reaction vessel were heated by electromagnetic induction heating to heat the magnesium chloride and magnesium in the reaction zone to a temperature of 1000° C. Magnesium chloride melted by the heating flowed into the gap between the wall of the reaction vessel and the titanium ingot to form an insulating layer which also exhibited a pressure sealing action.

The reaction vessel was then pressurised to about 50atms. Immediately after such conditions were attained, titanium tetrachloride and liquid magnesium kept at 800° C were supplied to the reaction vessel at feed rates of 4.0l/min (7.0kg/min) and 1.2l/min (1.8kg/min), respectively. This caused the temperature of the bath to rise rapidly to 1827° C, and so the power for the electromagnetic induction heating was decreased to keep the temperature of 1827° C  $\pm$  50° C.

Subsequently, the ingot was drawn out downwardly at an average velocity of 1.3cm/min. The operation was continued for 2 hours, resulting in titanium ingot being manufactured in an amount of 0.2 tonne.

The magnesium chloride by-product produced during the operation was continuously discharged from the reaction vessel at the appropriate rate to keep the depth of the bath in the reaction vessel constant.

The titanium ingot so produced was compared to sponge titanium produced by the Kroll process. It was found that the titanium ingot had a high purity and quality similar to that shown in Table 1.

**Claims**

1. A method for producing titanium by the reduction of titanium tetrachloride with a reducing metal agent characterised by the steps of: maintaining the temperature and pressure in a reaction zone (12) in a reaction vessel (3) above the melting point of the metallic titanium (14) to be produced and above the vapour pressure of the reducing metal agent at that temperature; supplying titanium tetrachloride and the reducing metal agent to the reaction vessel (3) to react to produce a metallic titanium product (14) and a chloride by-product (13) of the reducing metal agent while maintaining the product and the by-product in a molten state; separating the metallic titanium product (14) and the chloride by-product (13) of the reducing metal agent from each by making use of the differences in their densities; collecting the metallic titanium product (14) at the bottom of the reaction vessel (3); and continuously drawing off the metallic titanium product (14) from the bottom of the reaction vessel (3).

2. A method as claimed in Claim 1 characterised in that the titanium product (14) is solidified by cooling as it is withdrawn.

3. A method as claimed in Claim 1 characterised in that a molten bath (12) of chloride of the reducing metal agent and optionally also of the reducing metal agent is previously formed in the reaction vessel so that the surface of the molten bath constitutes the reaction zone and titanium tetrachloride and the reducing metal agent are supplied to the reaction zone.

4. A method as claimed in Claim 3, characterised in that the titanium tetrachloride is supplied as a liquid from the top of the reaction vessel (3) and the reducing metal agent is supplied either in the same way or is injected into the bath (12).

5. A method as claimed in any preceding claim characterised in that the chloride by-product (13) of the reducing metal agent is discharged (9) from the reaction vessel at a rate arranged to maintain the position of the reaction zone (12) substantially constant.

6. A method as claimed in any preceding claim characterised by the steps of inserting a titanium ingot (11) into the bottom of the reaction vessel (3) resulting in the coalescence of the metallic titanium metal product (14) with the titanium ingot (11) and drawing the metallic titanium product (14) out continuously together with the titanium ingot (11) at a rate corresponding to the amount of the metallic titanium product being coalesced with the titanium ingot.

7. A method as claimed in any preceding claim characterised in that the reducing metal agent is magnesium or sodium.

8. A method as claimed in any preceding claim, characterised in that the reaction pressure is above the total sum of the vapour pressures of the reducing metal agent and its chloride at the reaction temperature.

9. A method for producing a metal by the reduction of a polyhalide of the metal with a reducing metal agent characterised by the steps of: maintaining the temperature and pressure in a reaction zone (12) in a reaction vessel (3) above the melting point of the metal (14) to be produced and above the vapour pressure of the reducing metal agent at that temperature; supplying the polyhalide of the product metal

and the reducing metal agent to the reaction vessel (3) to react to produce the product metal (14) and a halide by-product (13) of the reducing metal agent while maintaining the product and the by-product in a molten state; separating the product metal (14) and the halide by-product (13) of the reducing metal agent from each by making use of the differences in their densities; collecting the product metal (14) at the bottom of the reaction vessel (3) and continuously drawing off the product metal (14) from the bottom of the reaction vessel (3).

10. An apparatus for producing metallic titanium by the reduction of titanium tetrachloride with a reducing metal agent characterised by: a reaction vessel (3) having a reaction zone (12) in which a temperature above a melting point of the titanium product (14) is defined and which is kept at a pressure sufficient to prevent boiling of the reducing metal agent and its chloride (13) at that temperature; a reducing metal agent feed pipe (6) for supplying the reducing metal agent in the form of a liquid from the side or the top of the reaction vessel (3) to the reaction zone; a titanium tetrachloride feed pipe (7) for supplying titanium tetrachloride from the top of the reaction vessel (3) to the reaction zone; a discharge pipe (9) for discharging the chloride by-product of the reducing metal agent from the side of the reaction vessel; heating means (8) positioned outside the reaction vessel (3) at a position corresponding to the reaction zone (12); and a withdrawal section (10) at the bottom of the reaction vessel (3) for continuously drawing out the metallic titanium product (14).

11. An apparatus as claimed in Claim 10 characterised in that the withdrawal section is a mould section (10) at the bottom of the reaction vessel (3) for solidifying the molten metallic titanium product (14) by cooling as it is continuously drawn out from the reaction vessel (3).

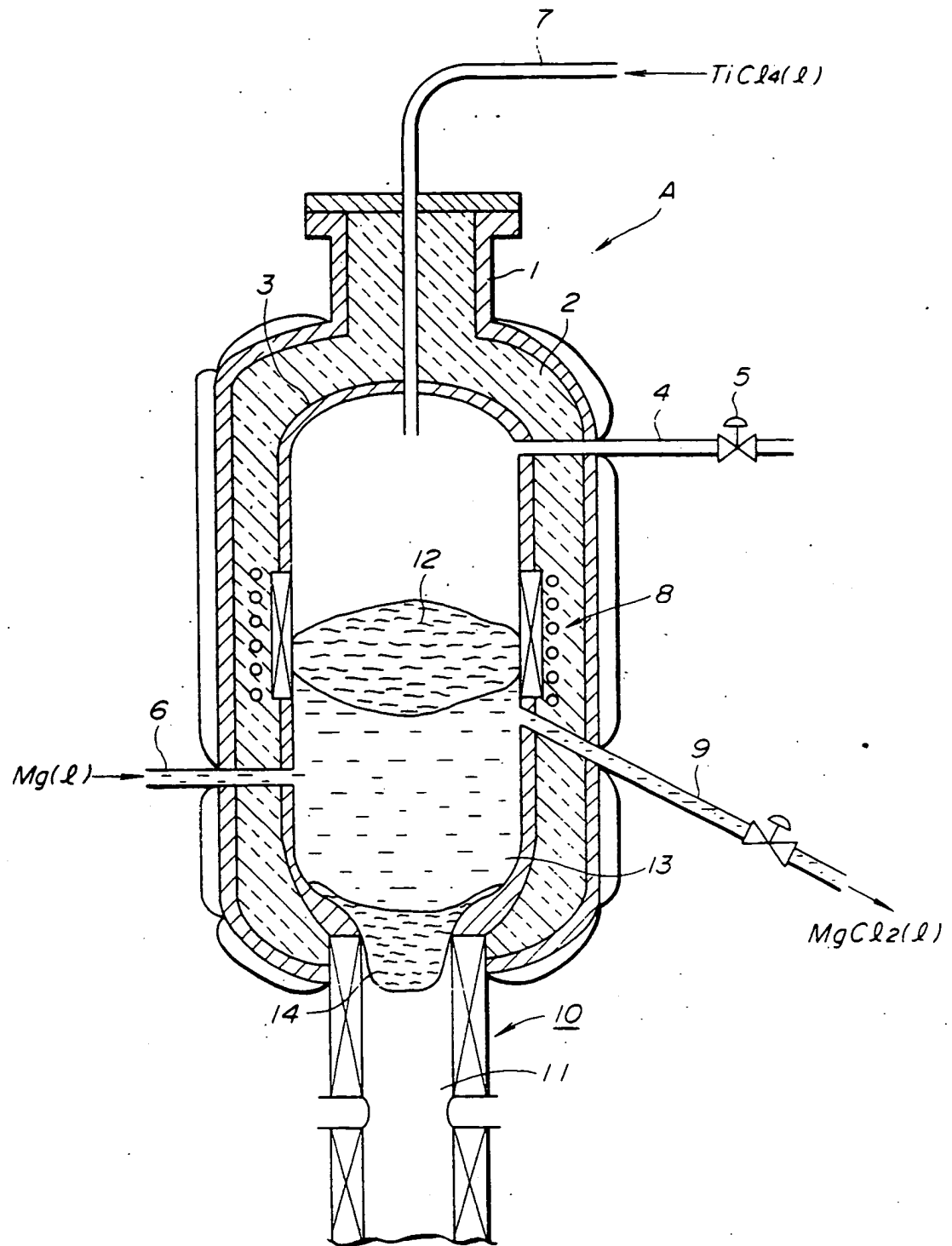
12. An apparatus as claimed in Claim 11 characterised by cooling means (33-35) located in the wall of the reaction vessel (3) for circulating a cooling agent at least from the reaction zone (12) to the mould section (10).

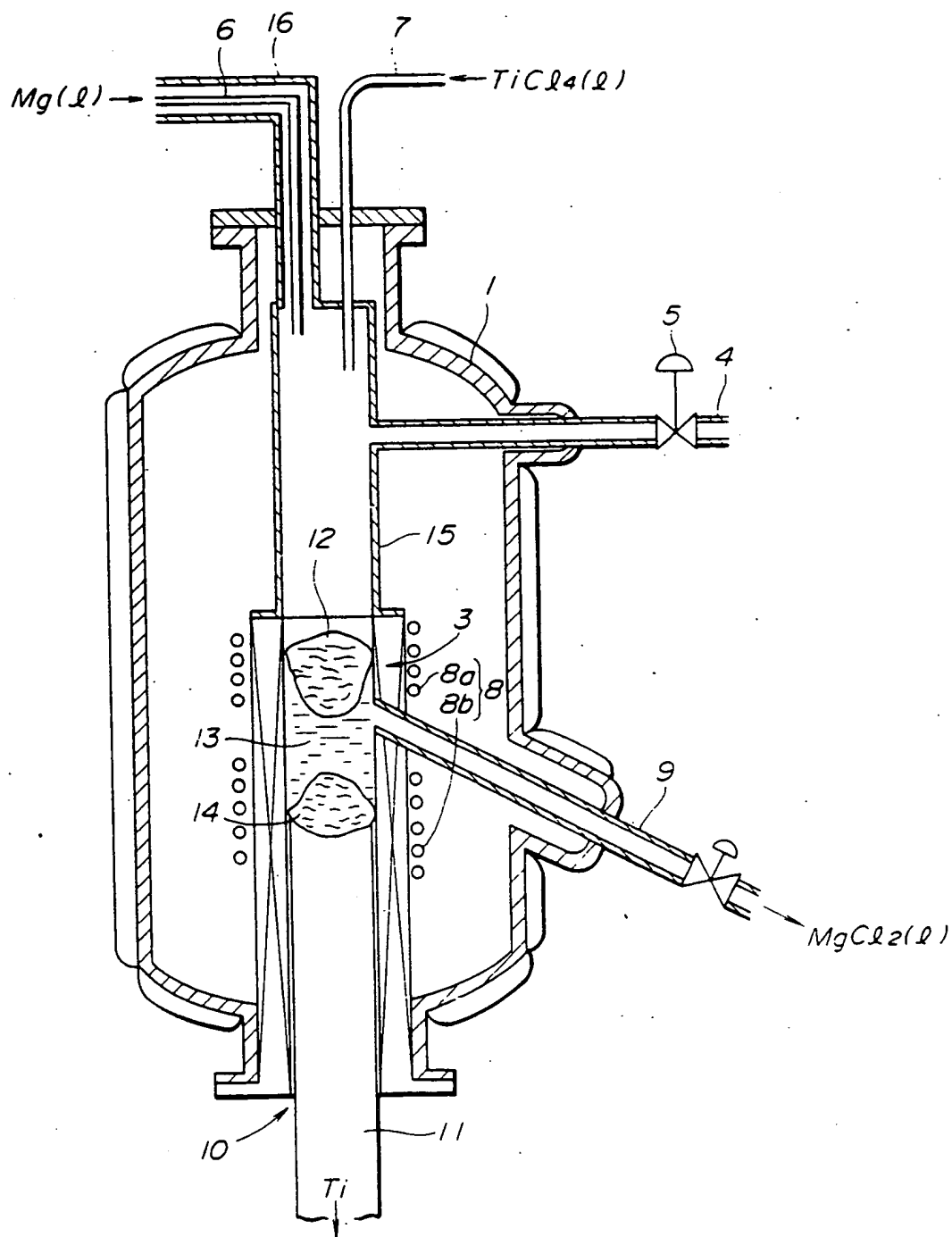
13. An apparatus as claimed in Claim 11 or Claim 12 characterised by heating means (8) arranged on portions of the outer periphery of the reaction vessel at positions corresponding to the reaction zone (12) and the mould section (10).

14. An apparatus as claimed in any of Claims 10 to 13 characterised in that the reaction vessel (3) comprises a plurality of longitudinal segments (22) separated by slits (31) thereby dividing the reaction vessel (3) in its longitudinal direction each of the slits (31) being filled with an electrically insulating and heat resistant material.

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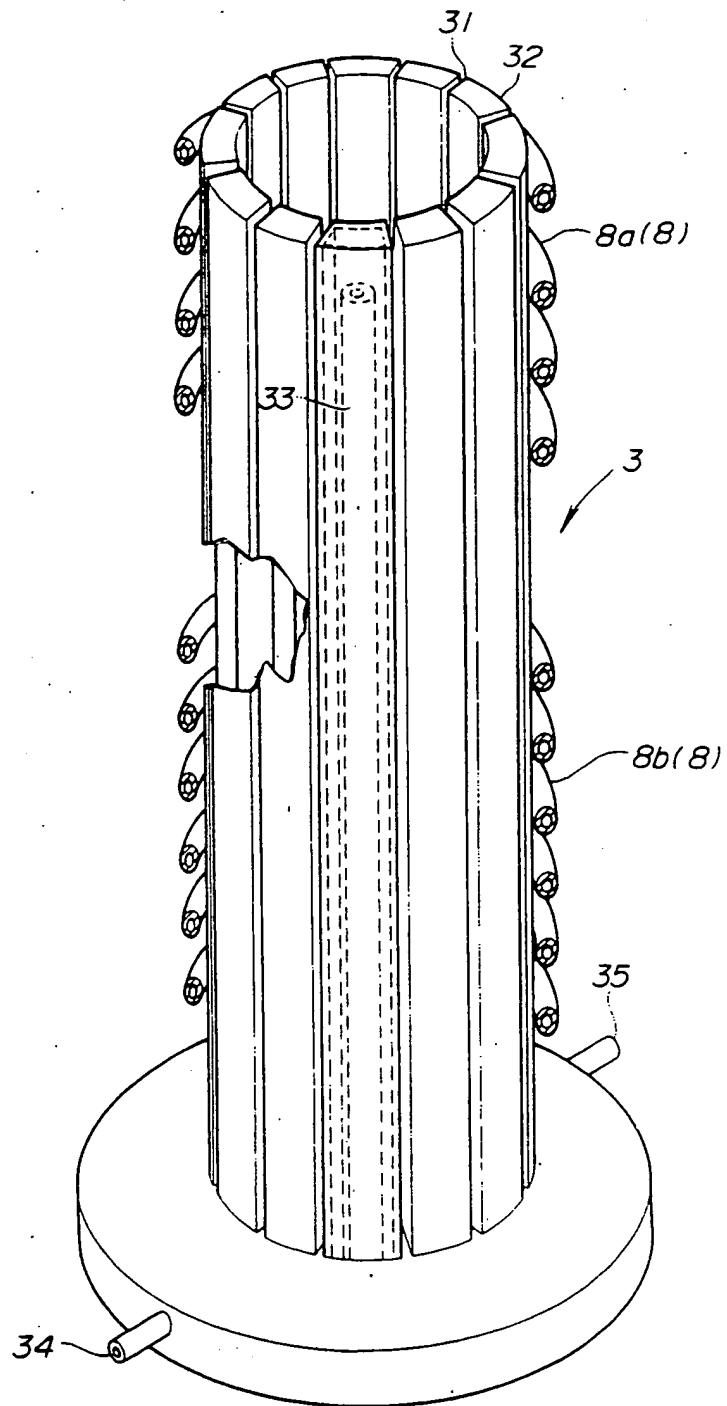
**FIG. 1**



**FIG. 2**

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**FIG. 3**





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# EUROPEAN SEARCH REPORT

Application Number

EP 88 30 6510

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-3 847 596 (G.W. HOLLAND et al.) * claim 1 * & JP - B - 46 19761 (Cat. D) ---	1,9	C 22 B 34/12 C 22 B 5/04
A	FR-A-2 461 014 (COCKERILL) * claim 1 * & JP - A - 56 35733 (Cat. D) ---	1	
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A	US-A-2 816 828 (M. BENEDICT et al.) ---		
A	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 228 (C-303)[1951], 13th September 1985; & Jp - A - 60 89529 (MITSUBISHI KINZOKU K.K.) 20-05-1985 ---		
A,D	US-A-3 775 091 (P.G. CLITES et al.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 22 B 34/12 C 22 B 5/04
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
BERLIN		29-08-1988	SUTOR W
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